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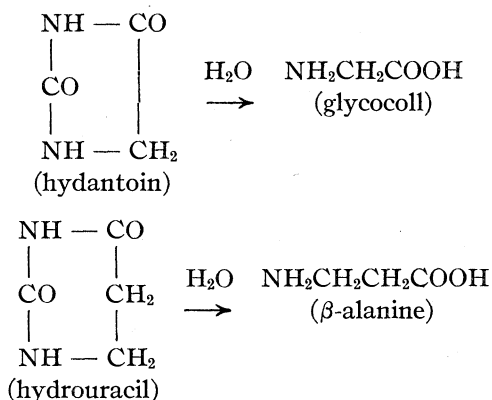
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aminoacids. The above relationships are expressed by the following equations:



Before undertaking our research on catalytic reductions we devised a practical machine whereby we might operate on a quantitative basis with large quantities of reagents. A description of this machine and a complete record of our preliminary work on uracil reduction will be published in a future number of the *Journal of the American Chemical Society*.

¹ *Ber.*, **45**, 1912 (619).

² *Ibid.*, **37**, 1904 (124); **38**, 1905 (1398, 1406).

³ *Ibid.*, **45**, 1912 (3579, 3595).

⁴ Lengfeld and Stieglitz, *Amer. Chem. J.*, **15**, 1893 (221).

⁵ *J. Biol. Chem.*, **3**, 1907 (183).

THE APPLICATION OF A DIFFERENTIAL THERMOMETER IN EBULLIOSCOPY

BY ALAN W. C. MENZIES AND SYDNEY L. WRIGHT

DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY

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For purposes of molecular weight determination of dissolved substances, the ebullioscopic procedure has certain advantages over the method of cryoscopy. Since, to use the latter, one must for convenience employ solvents whose freezing-points lie at easily accessible temperatures, it comes about that water, benzene and acetic acid have been commonly preferred. To obtain satisfactory values for the molecular weight of a solute, it is best to choose a solvent so alike to it chemically that compound formation between them shall be at a minimum. To be restricted in the choice of solvents is, therefore, a disadvantage. Boiling temperatures are preferable to freezing temperatures as disfavoring the formation of exothermic compounds. A majority of organic compounds boil nor-

mally below 300°C . If, as is true, the solvent must differ by at least 150 degrees in boiling-point from the solute in order that the volatility of the latter shall not vitiate the results, then the use is indicated of such solvents as boil below about 100° , and these solvents are indeed those most commonly used. The low solubility of certain solutes at the freezing-points of the available solvents is a factor against cryoscopy. On the other hand, the precision attainable in cryoscopy has, in the past, been considerably greater than that realized in ebullioscopy, even with apparatus fortified against error by the superimposition of a multiplicity of paraphernalia.

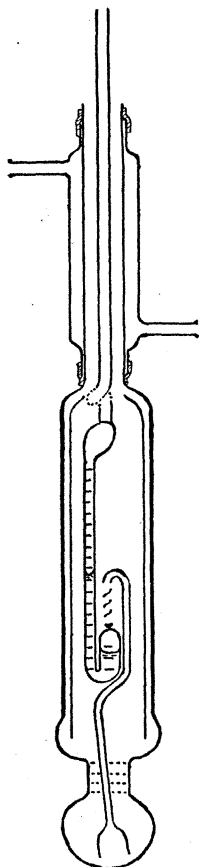


FIG. 1

For these and other reasons, a very great deal of work has been carried out by very many investigators with a view to improving the ebullioscopic technique. One may but mention the two dozen papers by Beckmann and his collaborators;¹ and the work of Hite,² Orndorff and Cameron,³ Jones,⁴ Ross Innes,⁵ Meyer and Desamari,⁶ Drucker,⁷ Sakurai,⁸ Landsberger,⁹ Walker and Lumsden,¹⁰ McCoy,¹² Smits,¹³ Rijber,¹⁴ Ludlam,¹⁵ Erdmann and Unruh,¹⁶ Lehner,¹⁷ Turner.¹⁸ Even a single publication by one writer—Hite—reports the trial of over 100 different forms of apparatus. In all these, and many other investigations, the bulb of a mercurial thermometer has been submerged beneath the surface of the boiling solution, and much of the work has been directed to the avoidance of the consequent irregular superheating. In our opinion, the two most successful improvements made since 1892 have originated in this country, the introduction, namely, by Bigelow¹⁹ of electric heating, and by Cottrell²⁰ of a “lift-pump” which pumps the solution over the bulb of the thermometer, which no longer need be submerged in the solution, but is located above the solution in the vapor phase. When Cottrell’s device is employed, there remain outstanding the errors inherent in the Beckmann type of thermometer, the error due to uncertainty as to actual concentration, and the very serious error due to change of boiling-point caused by change of barometric pressure during the observations. This last may, in part at least, be overcome by the employment of somewhat cumbrous “manostats,”²¹ by especially constructed aneroid barometers,⁶ or by the use of a second, duplicate, apparatus²² operated simultaneously and containing another Beckmann thermometer immersed in the pure boiling solvent.

In 1910, Menzies²³ had described a simple apparatus, independent of

barometric change, which gives molecular weights of solutes at their boiling-points by direct measurement of lowering of vapor pressure, without the use of any thermometer. Continuing this effort at simplification, he found that the application of the differential thermometer of the preceding article to ebullioscopy with the Beckmann type of apparatus served only to render more glaring the inevitable irregularities inseparable from that method of procedure. When, however, Cottrell's paper appeared in 1919, the first opportunity was taken to secure collaboration in working out the simplest possible apparatus and technique which should free ebullioscopy from all its most serious drawbacks.

The diagram, fig. 1, shows a boiling tube, whose narrowed upper portion itself serves as condenser tube. A glass cylinder, open above and below and of diameter slightly less than the boiling tube itself, is located concentrically within the latter, and confers the advantages of a double jacket. Within this is supported the differential thermometer, on the lower bulb of which hangs the pump, loosely, as a hat on a peg.²⁴ The absence of rigid connection diminishes breakage, besides adding flexibility, literal and metaphorical. The boiling tube is heated by a common Bunsen burner, with a low flame protected by the customary metal draught-shield. When boiling begins, portions of the liquid in the bulb are carried by the vapor in fragments up the pump and discharged to form a thin film over the lower bulb of the thermometer, which thus attains the temperature at which this liquid, or solution, is in equilibrium with the vapor. The upper bulb acquires the temperature of the pure boiling solvent. The thermometer registers the difference between these two temperatures. Equilibrium is reached so rapidly that fresh additions of solute may be made as fast as they can be weighed out. Contrary to all ebullioscopic tradition, the apparatus will give good results in a room that is not free from draughts. Unlike every other ebullioscopic apparatus, this form is entirely free from all corks, ground glass joints or stoppers.

The sources of error, especially that due to barometric change, eliminated by the use of the new type of differential thermometer have been briefly referred to in the preceding article. The advantages gained by removing the lower bulb from immersion in the boiling liquid have been well explained by Cottrell²⁰ and confirmed by Washburn and Read.²⁵ The chief residual source of error lies in the uncertainty as to the true concentration of the boiling solution as deduced, not by subsequent analysis, but simply from the weights of solvent and solute used. Part of the solvent is absent from the solution in the form of condensate on the walls, and part is absent in the form of vapor. This source of error, ever present in the Beckmann type of apparatus, has often failed of due consideration. To minimize it, we constrict the boiling tube above the lower bulb, mark cc. graduations on the cylindrical neck so developed, and read off the actual working volume of the solvent an instant after causing ebullition to cease, while

the tube is still wet with condensate and filled with vapor.

A simple water-filled differential thermometer suffices for the range of temperature from the boiling-point of water to that of ether, thus embracing the use of such other solvents as carbon bisulphide; acetone; chloroform; methyl, ethyl and propyl alcohols; ethyl formate, acetate and iodide; carbon tetrachloride and benzene; and allowing a choice adequate for ordinary purposes. No "setting" of the thermometer for the use of different liquids is required.

Details of procedure and of results will be given in more complete publications elsewhere. Different sets of determinations with the same materials, carried out on different days, yield results concordant within one-half of one per cent. In spite of the simplicity of the apparatus, we venture to think that this form of the ebullioscopic method compares favorably with the customary form of the cryoscopic method in ease and speed of operation as well as in precision of results.

¹ References to the numerous papers of Beckmann and his collaborators may be found in the work of Jellinek, C., *Stuttgart, Lehrbuch der Physikalischen Chemie*, **2**, 1915 (783 et seq.).

² Hite, *Baltimore, Md., Amer. Chem. J.*, **17**, 1895 (514).

³ Orndorff and Cameron, *Ibid.*, **17**, 1895 (517).

⁴ Jones, H. C., *Easton, Pa., The Freezing-Point, Boiling-Point and Conductivity Methods*, 1912.

⁵ Innes, R., *London, J. Chem. Soc.*, **81**, 1902 (682).

⁶ Meyer and Desamari, *Berlin, Ber. deut. Chem. Ges.*, **42**, 1909 (797).

⁷ Drucker, *Leipzig, Z. phys. Chem.*, **74**, 1910 (612).

⁸ Sakurai, *London, J. Chem. Soc.*, **61**, 1892 (989).

⁹ Landsberger, *Berlin, Ber. deut. Chem. Ges.*, **31**, 1898 (461).

¹⁰ Walker and Lumsden, *London, J. Chem. Soc.*, **73**, 1898 (502).

¹² McCoy, H., *Baltimore, Md., Amer. Chem. J.*, **23**, 1900 (502).

¹³ Smits, A., *Amsterdam, Proc. Akad. Wetens.*, **3**, 1900 (86).

¹⁴ Rijber, *Berlin, Ber. deut. Chem. Ges.*, **34**, 901 (1060).

¹⁶ Ludlam, *London, J. Chem. Soc.*, **81**, 1902 (1193).

¹⁶ Erdmann and Unruh, *Hamburg, Z. anorg. Chem.*, **32**, 1902 (413).

¹⁷ Lehner, *Berlin, Ber. deut. Chem. Ges.*, **36**, 1903 (1104).

¹⁸ Turner, *London, J. Chem. Soc.*, **97**, 1910 (1184).

¹⁹ Bigelow, *Baltimore, Md., Amer. Chem. J.*, **22**, 1899 (280).

²⁰ Cottrell, *Easton, Pa., J. Amer. Chem. Soc.*, **41**, 1919 (721).

²¹ Smits, A., *Leipzig, Z. phys. Chem.*, **39**, 1902 (415); Burt, *London, J. Chem. Soc.*, **85**, 1904 (339); Drucker, *loc. cit.*; Beckmann, *Leipzig, Z. phys. Chem.*, **79**, 1912 (565); etc.

²² Beckmann, *loc. cit.*; Washburn and Read, *Easton, Pa., J. Amer. Chem. Soc.*, **41**, 1919 (729); Sluiter, *Amsterdam, Proc. Akad. Wet.*, **17**, 1914 (1043).

²³ Menzies, A. W. C., *Easton, Pa., J. Amer. Chem. Soc.*, **32**, 1910 (1615).

²⁴ The complete apparatus, with both boiling-tube and water-filled thermometer of Pyrex glass, is furnished by Messrs. Eimer and Amend, 205 Third Avenue, New York, N. Y.

²⁵ Washburn and Read, *vide note 22, supra*.